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METHOD AND INSTALLATION FOR MAKING AN OPTICAL FIBRE

The present invention relates to a process for the manufacture of an optical fiber made of polymers with
5 low transmission losses, this fiber comprising a core and a sheath, the core being formed from a first polymer based on methyl methacrylate and optionally on another (meth)acrylic ester and the sheath being formed
10 from a second polymer having a lower refractive index than that of the core.

The present invention also relates to a plant for the implementation of this process.

15 One of the problems encountered by manufacturers of optical fibers made of polymers is that of reducing to a minimum the amount of defects, impurities and dusts in the core polymer, as they absorb or scatter light and thus accentuate the weakening of the light
20 transmitted in the optical fiber.

A known process for the manufacture of an optical fiber made of polymers consists first in preparing a solid cylindrical rod formed from a first polymer based on
25 methyl methacrylate and then secondly in melt fiberizing this solid cylindrical rod by extrusion. The second polymer, which acts to form the sheath of the optical fiber, can be applied by coextrusion or coating from a solution.

30 Such a process is disclosed in particular in French patent No. 2 405 806. One of the difficulties of such a process is the production of a solid cylinder of the polymer of the core, which is prepared by radical bulk
35 polymerization of purified methyl methacrylate. Complete control of the polymerization and in particular of the exchanges of heat is essential in order to prevent any formation of bubbles.

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Another known process for the manufacture of an optical fiber made of polymers consists of a continuous process according to which the monomers for forming the core of the fiber, essentially methyl methacrylate, the polymerization initiator and the chain-transfer agent are distilled and purified under sealed or leaktight conditions. A polymerization vessel is subsequently filled with the materials thus distilled, and the radical bulk polymerization is carried out by heating under reduced pressure.

The resulting polymer, the temperature of which is not lowered to the glass transition temperature or less, is continuously conveyed to a spinning device in order to subsequently obtain a fiber.

Such a process is disclosed in particular in French patent No. 2 493 997.

As in the preceding process, the radical bulk polymerization has to be fully and precisely controlled. This is because the control temperature is in this instance particularly important as the radical bulk polymerization of methyl methacrylate is highly exothermic and can dangerously accelerate. At the industrial level, the exothermicity of the polymerization reaction causes safety problems which are complex to manage.

However, despite the abovementioned disadvantages of the radical bulk polymerization of methyl methacrylate, this type of polymerization is currently recommended in numerous publications and is preferred to the aqueous suspension polymerization of methyl methacrylate.

Thus, according to French patent No. 2 493 997, the preparation by suspension polymerization of the core of the optical fiber made of poly(methyl methacrylate) requires a large amount of water, the resulting polymer

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More specifically, a subject matter of the present invention is a batchwise process for the manufacture of an optical fiber made of polymers, this fiber comprising a core and a sheath, the core being formed from a first polymer based on methyl methacrylate and optionally on a (meth)acrylic ester other than methyl methacrylate and the sheath being formed from a second polymer having a lower refractive index than that of the core.

The process according to the invention is characterized in that it is implemented in an in-line plant ranging from a device for the purification of the starting materials to a spinning device, involving the intermediacy of the various devices of the in-line plant and the various transfer means connecting the various devices of the in-line plant, this plant being leaktight to the external air and to dust and sheltered from light, in particular ultraviolet radiation.

In addition, the process according to the invention comprises the following stages:

(1) beads of the first polymer are prepared by suspension polymerization of purified methyl methacrylate and optionally of at least one purified (meth)acrylic ester other than methyl methacrylate in demineralized, filtered and deoxygenated water, the polymerization being carried out in the presence of at least one radical polymerization initiating agent, of at least one chain-transfer agent and of at least one suspending agent and in the virtually complete absence of polymerization inhibitor and of impurities, such as:

(a) biacetyl, in an amount reduced to at most 1 ppm with respect to the total amount of

5 (b) transition metal ions capable of giving strong light absorption in the visible region;

the polymerization also being carried out with
15 stirring, under an atmosphere of an inert and
dedusted gas;

25 (3) at least a portion of the beads obtained on
conclusion of stage (2) is transferred, under an
atmosphere of a dedusted and preferably inert gas,
from the intermediate tank or tanks to a
coextrusion device and the core of the fiber,
30 starting from said beads, and the sheath of the
fiber, starting from a polymer having a lower
refractive index than that of the core, are
coextruded;

35 (4) the fiber obtained at the outlet of the
coextrusion device is cooled in a gradual and
controlled fashion, so as to avoid quenching the
first polymer constituting the core of the fiber,
and the fiber is drawn, in order to obtain a fiber

A first important characteristic of the process according to the invention is its batchwise nature by virtue of the presence of at least one intermediate tank provided for the beads of the first polymer based on methyl methacrylate and optionally on a (meth)acrylic ester other than methyl methacrylate.

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a dedusted gas is valid throughout the description of the present invention.

5 A third important characteristic of the process according to the invention is the fact that an aqueous suspension polymerization is used to prepare the beads of the first polymer used to prepare the core of the optical fiber. To do this, use is made of water which is simultaneously demineralized, filtered and
10 deoxygenated, in order to achieve the degrees of purity (a), (b) and (c) mentioned above in the general definition of the process according to the invention.

15 Surprisingly, it has been found that it is possible to manufacture an optical fiber having excellent optical transmission characteristics if all the operating conditions set out in claim 1 and restated above are observed.

20 Preferably, the purification is also carried out of at least one of the agents used in the implementation of the aqueous suspension polymerization reaction, more preferably of all the agents used, as follows:

25 - the polymerization initiating agent is purified either by distillation or by recrystallization, the operation being carried out under an atmosphere of an inert and dedusted gas, and the purified polymerization initiating agent is
30 transferred into the polymerization reactor via means leaktight to the external air and to dust while maintaining this agent under an atmosphere of an inert and dedusted gas;

35 - the chain-transfer agent is purified by distillation, the operation being carried out under an atmosphere of an inert and dedusted gas, and the distilled chain-transfer agent is transferred into the polymerization reactor via

5 - the suspending agent is purified by
recrystallization, the operation being carried out
under an atmosphere of an inert and dedusted gas,
and the recrystallized suspending agent is
transferred into the polymerization reactor via
10 means leaktight to the external air and to dust
while maintaining this agent under an atmosphere
of an inert and dedusted gas.

Use may be made, to prepare the first polymer, as (meth)acrylic ester other than methyl methacrylate, of one or more monomers chosen from the group consisting of ethyl acrylate, ethyl methacrylate, methyl acrylate, propyl acrylate, propyl methacrylate, butyl acrylate and butyl methacrylate.

It is desirable to use, as polymerization initiating agent, an agent which promotes the production of an optical fiber having low transmission losses in the

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region of visible light and having decomposition temperatures of less than 110°C. In this respect, mention may be made of polymerization initiating agents of azo type, such as 2,2'-azobisisobutyronitrile, known
5 for its high degree of purity, its relatively weak influence in the visible region and its optimum operating temperature of between 50 and 80°C.

The abovementioned polymerization initiating agents can
10 be combined with others having decomposition temperatures of greater than 110°C. In this respect, mention may be made of compounds of alkylazo type, such as azo-tert-butane, azo-n-butane, azoisopropane and azo-n-propane.

15 Mention may be made, as chain-transfer agents suitable for the process according to the invention, of compounds of the family of the linear mercaptans, such as n-butyl mercaptan, n-propyl mercaptan or n-dodecyl
20 mercaptan; compounds of the family of the secondary mercaptans, such as isopropyl mercaptan, or compounds of the family of the tertiary mercaptans, such as tert-butyl mercaptan.

25 Mention may be made, as suspending agents suitable for the process according to the invention, of poly(vinyl alcohol)s with a degree of hydrolysis at least equal to 75%, preferably 85-90%; cellulose ethers, such as hydroxyethylcellulose; tribasic calcium phosphate; or
30 acrylic or methacrylic acid homopolymers or copolymers of at least 50% by weight of these acids with comonomers which can copolymerize with them, in particular methyl methacrylate, these homo- or copolymers preferably being used in the form of alkali
35 metal salts or ammonium salts or else in their form neutralized with disodium phosphate. Use is preferably made, among the abovementioned suspending agents, of salified homo- and copolymers because of their

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hydrophilic nature, which facilitates their removal when the beads of the first polymer are washed.

5 In accordance with a preferred alternative form of the process according to the invention, the various starting materials used in the preparation of the first polymer, namely the demineralized and dedusted water, the purified monomers and the suspending, chain-transfer and polymerization initiating agents, are
10 introduced separately into hermetically closed vessels flushed with an inert gas. These vessels are connected directly to the polymerization reactor with, as intermediate, a metering device for each vessel. In addition, the introduction of the materials into the
15 polymerization reactor is preferably carried out according to the following stages:

- first, a predetermined amount of demineralized and dedusted water originating directly from a system
20 for the production of ultrapure water is introduced into the reactor and then a suspending agent in solution in water, filtered at a threshold of $0.1 \mu\text{m}$ into the metering chamber, advantageously via a septum, is introduced, the
25 suspending agent advantageously being introduced by imposing a pressure in the reactor slightly below atmospheric pressure. This water is heated to the polymerization temperature and, simultaneously, an inert gas, preferably nitrogen,
30 is bubbled therein in order to remove the oxygen dissolved in the water. This stage is generally fairly long and can last several hours;

- subsequently, the entire organic phase, comprising
35 the purified monomers, the chain-transfer agent and the polymerization initiator or initiators, are introduced into the reactor via a filter with a porosity of $0.1 \mu\text{m}$, for example by propelling with dedusted nitrogen; the entire organic phase,

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including the polymerization initiator, is added, preferably all at once;

- the reaction mixture is stirred under somewhat turbulent conditions.

The suspension polymerization reaction is advantageously carried out under a pressure substantially equal to atmospheric pressure or slightly greater. The temperature in the polymerization reactor can vary from 50°C to 110°C.

The polymerization reaction is carried out so that the level of residual monomers is as low as possible, preferably less than 2 mol% of the total of the monomers used in the implementation of this polymerization.

The suspension polymerization is advantageously carried out in order to prepare a first polymer, in the form of beads, the weight molecular mass (\overline{M}_w) of which varies from 100 000 to 200 000 with a polydispersity (P) of the order of 2.

On conclusion of the polymerization reaction, the beads obtained of the first polymer are separated and washed using demineralized and dedusted water and the beads are dried under an atmosphere of a dedusted gas (that is to say devoid of dust or of particles with a diameter equal to or greater than 0.1 μm) and, under this atmosphere, the dried beads are stored in at least one intermediate tank.

The intermediate tank (or tanks) can also be the thermostatically-controlled chamber used to dry the beads of the first polymer.

The beads of the first polymer which are obtained on conclusion of the polymerization reaction are

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Preferably, the extrusion of the first polymer used to prepare the core of the optical fiber is carried out at a temperature not exceeding 280°C.

- 5 At the outlet of the coextrusion device, in the die, the temperature is generally of the order of 220-250°C.

For the overall automatic control of the coextrusion line, and in order to ensure that the final diameter of
10 the fiber is even, the operation will preferably be carried out in the following way:

- a first automatic control, taking into account the temperatures of the various parts of the extruder,
15 the pressures and the rotational speeds of the screws, which makes it possible to provide a constant material throughput at the outlet of the die head;
- 20 - a second automatic control which makes it possible to ensure that the final diameter of the fiber is even: automatic control of the drawing rate by continuous measurement of the diameter in a region where the fiber has reached a temperature of
25 approximately 80°C.

It is possible, by operating in this way, to eliminate the critical region where the material is in an elastic phase, which can lead to a pumping region with high
30 oscillations and thus very significant variations in diameters.

The optical fiber exiting from the coextrusion device is gradually cooled, avoiding a sudden fall in the
35 temperature of the optical fiber which might damage its mechanical and optical properties by a quenching effect.

In order to gradually cool the optical fiber exiting from the spinning device, use is preferably made of one or other of the two following methods:

5 First method: the optical fiber is cooled using a gas stream and then using temperature regulated water, by sprinkling, spraying and/or immersion. Cooling using a gas stream is preferably carried out inside a protective column surrounding the fiber in order to
10 prevent disturbance to the fiber which would risk modifying its geometry, in particular its diameter. More preferably, the protective column is composed of several successive units with a passage for the optical fiber, each of these units being heated at a
15 temperature which decreases with distance from the spinning device: this makes it possible to provide gradual, slow and controlled cooling of the optical fiber until a temperature is obtained which is sufficiently low to carry out the cooling with water
20 without the risk of quenching.

Second method: the fiber is cooled using temperature regulated water, so as not to lead to a sudden fall in the temperature of the fiber, by sprinkling, spraying
25 and/or immersion.

At the same time as the optical fiber is gradually cooled, it is drawn while avoiding an excessively high draw ratio which might lead to an excessively high
30 orientation of the macromolecular chains.

Preferably, the draw ratio imposed varies from 1.5 to 6, better still from 2 to 4 (the draw ratio corresponds to the ratio of the square of the diameter of the die
35 to the square of the diameter of the optical fiber).

Another subject-matter of the present invention is an in-line plant for the implementation of the abovementioned process.

This in-line plant exhibits the following characteristics:

- 5 - it is entirely leaktight to the external air
and to dust and sheltered from light, in
particular ultraviolet radiation. To achieve
this, the plant is in its entirety isolated
from the external environment.
- 10 - it comprises:
 - means for purifying the methyl methacrylate
and, if appropriate, means for purifying at
15 least one (meth)acrylic ester other than
methyl methacrylate, these purification means
having to make it possible to virtually
completely remove the polymerization
inhibitor and impurities, such as:
 - 20 (a) biacetyl, in an amount reduced to at
most 1 ppm with respect to the total
amount of monomers introduced into the
polymerization reactor,
 - 25 (b) transition metal ions capable of giving
strong light absorption in the visible
region,
 - 30 (c) dust or particles, the various
abovementioned starting materials used
in the suspension polymerization having,
if necessary, been filtered before
polymerization with a filtration
35 threshold of 0.1 micron;
 - at least one reactor for the suspension
polymerization of methyl methacrylate and
optionally of at least one (meth)acrylic

- means for separating the polymer obtained in the form of beads in the aqueous suspension polymerization reactor;

- means for washing the beads with demineralized and dedusted water;

- optionally means making it possible to eliminate the static electricity of the beads;

- means for transferring the beads from the polymerization reactor, involving the intermediacy of the washing, drying and storing means, to the coextrusion device;

- at least one extruder: depending upon the situation, a screw extruder equipped with a degassing region, for

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forming the core of the optical fiber,
or two successive extruders with a
degassing region provided between the
two extruders;

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• and a screw extruder for melting and
kneading the second polymer used to
form the sheath of the optical fiber;

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and a device for spinning a composite of
the core-in-sheath type;

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- means making it possible to cool, in a
gradual and controlled fashion, the
optical fiber exiting from the coextrusion
plant;

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- means for drawing the optical fiber in
order to achieve a total mean fiber
diameter ranging from 250 to 2 000
microns.

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Advantageously, the means for purifying the methyl
methacrylate and, if appropriate, at least one
(meth)acrylic ester other than methyl methacrylate
successively comprise:

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- a filter composed of a bed of basic and
activated alumina, preferably under an
atmosphere of an inert and dedusted gas, in
order to at least partially remove the
compounds possessing labile hydrogen, the
highly polar compounds, such as biacetyl, and
the polymerization inhibitor;

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- at least one device for distillation under
partial vacuum and under an atmosphere of an
inert and dedusted gas, in order to remove

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virtually all the polymerization inhibitor, the biacetyl and the transition metal ions;

- and a filter which makes it possible to remove
5 virtually all the particles or dust with a mean diameter of greater than or equal to 0.1 μm .

An example of a coextrusion device suitable for the implementation of the process according to the
10 invention is represented in the single figure appended to the description.

Generally, this device comprises at least one extruder (1) provided with a degassing region for the beads of
15 the first polymer used to form the core of the optical fiber and one extruder (2) for forming the sheath of the optical fiber in the device (3) for spinning a composite of core-in-sheath type.

20 The optical fiber (4) exiting from the spinning device (3) is cooled in a gradual and controlled fashion so as to avoid quenching the first polymer constituting the core of the fiber:

- 25 - first, in a cooling region (5) having the form of a vertical passage, with air or an inert gas;
- secondly, in a region for cooling (6) using
30 temperature regulated water, by sprinkling and/or spraying and/or immersion.

At the same time as the cooling in the regions (5) and (6), the optical fiber is subjected to drawing under
35 the abovementioned conditions.

The optical fiber is finally wound off and stored on the roller (7).

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The scope of the present invention should not be restricted to the abovementioned alternative embodiments and encompasses any plant which makes possible the implementation of the process according to
5 the invention.